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**Agent and Method for Sealing or Consolidating Rock, Loose Rock or
Soils, Especially Boreholes**

This invention relates to a composition and a process for sealing or consolidating rock, mantle rock or soils and to the use for this purpose of certain silica sols containing hardness stabilizers.

The consolidation or sealing of rock, mantle rock or soils is a measure regularly necessary in construction engineering, for example for underpinning buildings, for sealing building pits or tips, in tunnel and canal construction and, above all, in geological exploration, such as the drilling of oil or natural gas pools. In the last of these applications, the sealing of wells is particularly important. Wells are sunk into the ground until a formation carrying oil, gas or - in well construction - water is reached. The well is stabilized against the formation by a cement casing. This cement casing is broken open at the bottom of the well so that the material to be brought up is able to pass freely from the formation into the well. Besides oil or gas, however, water also enters the well and has to be removed from the oil/gas by elaborate processes. Accordingly, efforts are made to minimize or avoid the penetration of water, so that the water-carrying parts of the formation are sealed off by suitable binders. However, consolidation or sealing is also a standard measure in the protection of agricultural land against wind or water erosion.

In general, binders, such as cement, bitumen, calcium salts or waterglass, are used in construction engineering. However, cement has the disadvantage that the particles are often not small enough to be able to penetrate into fine cracks or pores, resulting in an unsatisfactory sealing or consolidating effect. Even the use of waterglasses (an aqueous solution of sodium silicate) or microsilicas (an aqueous dispersion of amorphous silicon dioxide) does not always produce the required sealing effect. Accordingly, EP 530 600 proposes the use of silica sols for sealing or

In A2
consolidation. Silica sols are colloidal solutions of amorphous silicon dioxide which has a particle size of 7 to 50 nm. These silica sols gel in the presence of certain electrolytes or in the event of changes in the pH of the aqueous sols. By crosslinking of the SiO₂ units, the gel becomes more
5 viscous until consolidation is complete. Electrolytes which initiate gelation are generally present in the material to be consolidated or sealed. They are preferably salts of aluminium, iron, calcium or magnesium. However, EP 0 530 600 A1 proposes using silica sols in combination with a calcium donor in order to achieve rapid conversion of the sol into the gel.

10 Now, applicants have found that, surprisingly, the use of silica sols does not always lead to the required sealing or consolidating effects. This is particularly the case in the sealing of wells against penetrating formation water. According to applicants' observations, a free water phase frequently occurs which is a sign that no gelation and hence no sealing has taken
15 place. Accordingly, without being confined to one particular theory, applicants assume that, in contrast to the teaching of EP 0 530 600 A1, the formation of alkaline earth metal silicates and, above all, calcium silicate can inhibit the gelation process. Accordingly, one of the problems addressed by the present invention was to provide a sealing or
20 consolidating process which could even be carried out in the presence of water containing alkaline earth metal ions.

In addition, it is often not desirable in the sealing of wells to achieve rapid solidification of the binder. The binder is transported under pressure to the bottom of the well through a suitable pipe and is forced into the
25 formation there. The effect of rapid solidification of the binder would be that the binder would also gel in the pipe itself which of course is not what is wanted. On the contrary, the gelling effect should be delayed to the extent that the entire binder is forced into the formation by flushing, for example with water, so that gelation and consolidation only occur in the required
30 places. Accordingly, another problem addressed by the present invention

was to provide a process for the delayed consolidation or sealing of rock, mantle rock or soils.

It has now surprisingly been found that a mixture of aqueous silica sol and certain inhibitors for Ca^{2+} ions solves the problems stated above.

5 In a first embodiment, the present invention relates to a water-based composition for sealing or consolidating rock, mantle rock or soils in contact with water containing Ca^{2+} ions, the composition containing 2 to 40% by weight of SiO_2 (dry matter, based on the composition) in the form of an aqueous silica sol and, in addition, hardness stabilizers from the class of
10 inorganic polyphosphates, phosphonic acids, aminoethylene phosphonic acids, phosphoric acid esters, phosphonocarboxylic acids and polycarboxylic acids or mixtures of these substances in concentrations of 0.01 to 400 ppm.

The compositions according to the invention are generally suitable
15 both for the consolidation and for the sealing of any type of rock, mantle rock or soils in contact with water containing Ca^{2+} ions. Typical applications include construction engineering, particularly tunnel and well construction, and geological exploration, more particularly the sealing of
20 wells, more precisely their walls, against penetrating formation water.

20 Besides water, the compositions according to the invention contain silica sols containing amorphous SiO_2 in quantities of 2 to 60% by weight, expressed as dry matter and based on the sol, as carrier liquid. However, silica sols containing 25 to 50% by weight amorphous SiO_2 are preferred for the compositions according to the invention. The amorphous SiO_2 is
25 present in the form of non-interlinked spherical individual particles surface-stabilized by hydroxyl groups. The average particle diameter is in the range from 1 to 150 nm, preferably in the range from 5 to 70 nm and more particularly in the range from 5 to 40 nm. The specific surface of the silica sols is in the range from 50 to 700 m^2/g , as measured by the BET method.
30 By virtue of the colloidal distribution of the particles, no sedimentation of

particles is observed with silica sols. Accordingly, the sols may be stored for years. Aqueous silica sols are generally used. However, amorphous SiO_2 may also be converted into sols in other solvents, for example acetone or short-chain organic alcohols, such as methanol, ethanol or propanol (cf. **Ullmanns Encyklopädie der Technischen Chemie, 4th Edition, Vol. 21, pages 456 to 463, Weinheim 1982**). However, the compositions according to the invention contain only aqueous silica sols.

The compositions according to the invention contain in all, i.e. including the water content of the silica sols, between 60 and 98% by weight and more particularly between 60 and 80% by weight of water which preferably contains only small amounts of electrolytes, for example between 0.001 and 0.1% by weight. The water is preferably free from electrolytes. Electrolytes in the present context are understood in particular to be cations of mono- and divalent alkali metal and alkaline earth metal ions, i.e. Na^+ , K^+ , Ca^+ and Mg^{2+} ions. Aqueous silica sols of the type described above are present in the compositions in quantities of 20 to 60% by weight. According to the invention, so-called hardness stabilizers are added to the mixture of silica sol and water in concentrations of 0.01 to 400 ppm. Hardness stabilizers are compounds which, in less than stoichiometric quantities known for the purpose, are capable of completely and permanently preventing the precipitation of hardness ions from supersaturated aqueous solutions. To this extent, it was surprising that the addition of these compounds only leads to delayed gelation of the silica sols but does not permanently suppress their gelation. Hardness ions are mainly alkaline earth metal ions, more particularly calcium and magnesium ions (threshold effect). Particulars can be found in **Römpps Chemie Lexikon, 9th Edition, Vol. 6, 1994, pages 5000 to 5002**.

The compositions according to the invention contain compounds from the class of inorganic polyphosphates, phosphonic acid, aminoethylene phosphonic acids, phosphoric acid esters,

phosphonocarboxylic acids and polycarboxylic acids or mixtures thereof as hardness stabilizers. Salts of these compounds are also suitable. Compositions containing hardness stabilizers from the group consisting of aminotris(methylenephosphonic acid), 1-hydroxyethane-1,1-diphosphonic acid, phosphonobutane tricarboxylic acid, polyacrylic acid, polyaspartic acid, polymaleic acid or derivatives thereof or mixtures of these compounds are particularly preferred. Compositions containing tetrakis-[(phosphonomethyl)-imino]-bis-[2,1-ethanediylnitrado-bis-methylene]-phosphonic acid and/or salts thereof as hardness stabilizers are most particularly preferred.

Preferred mixtures of these stabilizers contain, for example, 1-hydroxyethane-1,1-diphosphonic acid sodium salt and polyacrylic acid or 1-hydroxyethane-1,1-diphosphonic acid sodium salt, aminotris(methylenephosphonic acid) and polyacrylic acid. The concentration in which the hardness stabilizers are used is between 0.01 and 400 ppm, more particularly in the range from 0.1 to 200 ppm and preferably in the range from 1 to 100 ppm, based on hardness stabilizer active substance.

In another embodiment, the present invention relates to a process for sealing or consolidating rock, mantle rock or soils in contact with water containing Ca^{2+} ions, in which the material to be consolidated or sealed is contacted with a solution containing aqueous silica sol and hardness stabilizers from the class of inorganic polyphosphates, phosphonic acids, aminoethylene phosphonic acids, phosphoric acid esters, phosphonocarboxylic acids and polycarboxylic acids or mixtures of these substances.

Aqueous silica sols containing 20 to 60% by weight SiO_2 (dry matter, based on the aqueous sol) are preferably used for this purpose. In general, the composition is forced under pressure into the material to be sealed or consolidated. The hardness stabilizers are then added during or after the treatment with the silica sol. They are preferably used in such quantities that the stabilizer concentration, based on the aqueous silica sol solution, is in the range from 0.01 to 400 ppm, preferably in the range from

0.1 to 200 ppm and more particularly in the range from 1 to 100 ppm.

In one particularly preferred embodiment, the process according to the invention is used for sealing underground formations, more particularly wells. To this end, the silica sol/water/stabilizer mixture is pumped through the feed pipe by suitable pumps to the bottom of the well, such a pressure being applied that the mixture penetrates deeply into the formation. This is followed by flushing with water until the mixture has been completely removed from the pipe. In this connection, the process according to the invention enjoys another advantage because the composition used only gels with a certain delay. Under the temperature, pH and pressure conditions at the bottom of the well, the composition preferably solidifies some 30 to 60 minutes after contacting with the material to be consolidated or sealed and hence with the water containing Ca^{2+} ions. The temperatures at the bottom of the well are normally in the range from 30 to 200°C, depending on the depth. The pressure is typically between 10 and 500 bar, again dependent on depth.

The most suitable stabilizer concentration can be selected in dependence upon the concentration of Ca^{2+} ions in the water with which the material to be consolidated or sealed is in contact. It has been found that the hardness stabilizers should preferably be present in the compositions according to the invention in such quantities that, based on a predetermined volume, the ratio by weight of Ca^{2+} ions to the hardness stabilizers is in the range from 0.5 to 5.0:1. The quantity of Ca^{2+} ions may readily be calculated through the determination of the water hardness.

The water in contact with the material to be consolidated or sealed generally has a content of Ca^{2+} ions of greater than 2 mmol/l and preferably greater than 4 mmol/l. Typical Ca^{2+} concentrations are in the range from 3 to 8 mmol/l. The pH of the formation water is generally in the acidic to mildly alkaline range, i.e. between 6 and 9. It has been found that a reduction in pH to values of 2 to 5 can generally prevent gelation.

Accordingly, the process according to the invention is preferably carried out at pH values of 6 to 9 or the composition according to the invention is preferably formulated by addition of acids or bases in such a way that its pH value is in the range mentioned.

- 5 The present invention also relates to the use of the compositions described in the foregoing for consolidating or sealing rock, mantle rock or soils in contact with water containing Ca^{2+} ions.

Examples

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The effectiveness of the process according to the invention was determined as follows: 11 g of a silica sol (Köstrosol® 0830 of Chemiewerk Bad Köstritz) were mixed with 40 g of deionized water and hardness stabilizers were subsequently added to the sol in various quantities. Between 0.7 and 1.0 ml of a calcium chloride solution (concentration of Ca^{2+} ions: 28,200 ppm) was then added dropwise to the resulting mixture, followed by heating for 15 minutes to 100°C. The vessel was left standing without stirring to cool. After 30 minutes, the degree of gelation was visually determined.

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The following evaluation was made:

100% solid	++
80 to almost 100% solid	+
less than 80% solid	-

The following hardness stabilizers were tested:

- A: 1-hydroxyethane-1,1-diphosphonic acid
25 B: amino-tris-(methylene phosphonic acid)
C: 1-hydroxyethane-1,1-diphosphonic acid disodium salt
D: mixture of B and C and polyacrylic acid

The stabilizers were used in the form of commercially available aqueous solutions (all products of Henkel KGaA):

- A: 60% by weight active substance (Turpinal® SL)
- B: 50% by weight active substance (Turpinal® D2)
- C: 10% by weight active substance (Turpinal® -2-NZ)
- D: 30% by weight active substance (Fostex® 617 B)

The quantities in Table 1 are based on active substance.

The results of the tests are set out in Table 1.

Table 1

No.	Stabilizer	Stabilizer concentration [ppm]	CaCl ₂ solution [ml]	Ca ²⁺ content in the solution [% by weight]	Ratio by weight Ca ²⁺ :stabilizer	Gelation after 30 mins.
1	A	0.1	0.8	0.04	0.7	++
2	A	0.2	0.8	0.04	1.0	++
3	B	0.3	0.8	0.04	1.4	+
4	B	0.3	0.7	0.04	2.0	++
5	C	0.7	1.0	0.06	1.3	++
6	C	0.7	1.0	0.06	1.5	+
7	D	0.7	1.0	0.06	4.0	++

Tests were also carried out at elevated temperature and pressure in order to simulate the conditions prevailing at the bottom of the well. Quantities of 5 g of a 50% by weight aqueous silica sol were diluted with 45 g of water and a certain ratio by weight of Ca²⁺ to SiO₂ was then adjusted by addition of a CaCl₂ solution (0.04% by weight Ca²⁺). The system was then heated for 30 minutes to 150°C in an autoclave under 10 bar pressure (nitrogen atmosphere) and left under those conditions for two hours. The results of the visual evaluation of the solutions are set out in Table 2.

Table 2

Solution	Ca:SiO ₂ [% by weight]	Effect
8	0.005	Thinly liquid
9	0.010	Slight gelation
10	0.020	Gelation
11	0.030	Gelation

Various quantities of stabilizer D were then added to solution 10 under the described conditions. It was found that the addition of 100 and 200 ppm of stabilizer resulted in delayed gelation after three hours. At higher concentrations, there was no sign of gelation. Accordingly, the process according to the invention leads to a desired delay in the gelation of the silica sol solutions, even at elevated temperature and pressure.